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The objective of these investigations was to study the magnetic properties of a collection of small magnetic particles or of a collection of magnetized domains with special attention given to the possibility of detecting and documenting the occurrence of spin tunneling and macroscopic quantum tunneling. Magnetized small particles are the basic elements used for magnetic storage, and our studies are important from a technological points of view: quantum-mechanical tunneling of the magnetization of small particles sets the ultimate limit on the reliability of magnetic storage and an upper limit on storage density.

Work done on this grant was both theoretical (Professor Eugene Chudnovsky of Lehman College) and experimental (Professor Sarachik and her group at City College), and also entailed active and on-going collaboration between the two. Our results are discussed below.

EXPERIMENT:

Using a Quantum Design magnetometer that was purchased with funds provided by the state of New York during the grant period, our experimental studies focussed on properties of magnetic molecules (Mn_{12} acetate complexes) and horse-spleen ferritin:

a) Studies of spin tunneling in molecular magnets: to appear in *Jour. Appl. Phys.* April 15, 1996; submitted to *Phys. Rev. Lett.*

Excellent experimental results were obtained in this area, which promises to be a very active field for its intrinsic, fundamental interest as well as the potential of important applications.

In contrast with most ensembles of small magnetic clusters, which are comprised of particles with various magnetic sizes and properties, a macroscopic sample of molecular magnets consists of a large number of chemically identical entities that are characterized by a unique set of parameters. This provides a unique opportunity for studying quantum tunneling. We have recently observed quantum-mechanical effects on a macroscopic scale in the magnetization of oriented crystals of Mn_{12} acetate complex which we attribute to thermally assisted, field-tuned resonant tunneling of magnetization between different quantum spin states in this

high-spin molecular magnet. We suggest that this observation in a sample of macroscopic size derives from tunneling in a large (Avogadro's) number of magnetically identical molecules. First synthesized by Lis (Acta Cryst. B 36, 2042 (1980)), $\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4$ contains four Mn^{+4} ($S=3/2$) ions in a central tetrahedron surrounded by eight Mn^{+3} ($S=2$) ions. Earlier experiments indicate an $S=10$ ground state (A. Caneschiet *et al.*, J. Am. Chem. Soc. 113, 5873 (1991)), suggesting a simple picture of the magnetic order with all the spins of one valence pointing up and of the other valence pointing down, as shown in the inset to Fig. 1.

For our experiments, powdered crystalline material was prepared by R. Ziolo of Xerox following the published procedures of Lis. It was allowed to set in epoxy in a 5.5 Tesla field, which served to orient the easy axes of all the crystallites in a common direction; this was confirmed visually

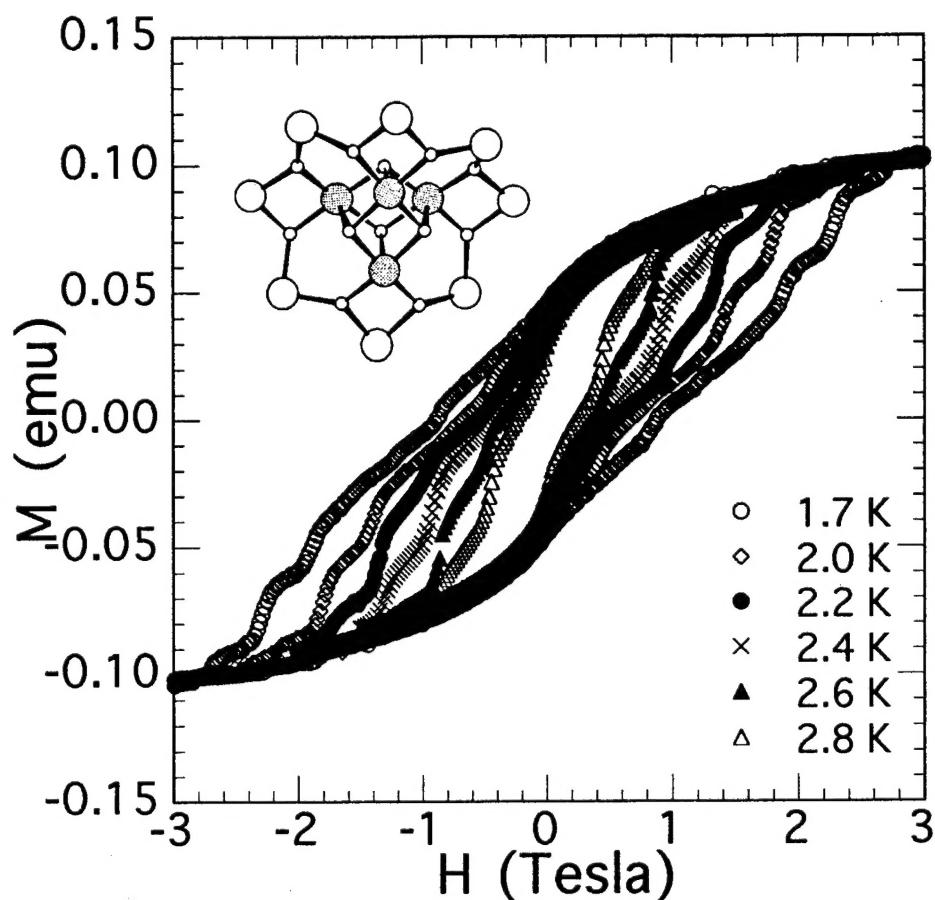


Figure 1

under a microscope. Fig. 1 shows the hysteresis loops obtained at different temperatures between 1.7 K and 2.8 K in a magnetic field applied along the easy axis. Steps that occur at specific value of magnetic field are clearly visible as the field is increased, while no such steps occur as the field is reduced back to zero. An orientationally disordered control sample exhibited no steps. We find further that the relaxation rate increases substantially when the magnetic field is tuned to a step.

We attribute this rather unexpected behavior to thermally assisted, field-tuned resonant magnetization tunneling between different quantum spin states in this high-spin molecular magnet. We propose a simple model, illustrated in Fig. 2. In zero field, the spin of the molecule has two degenerate

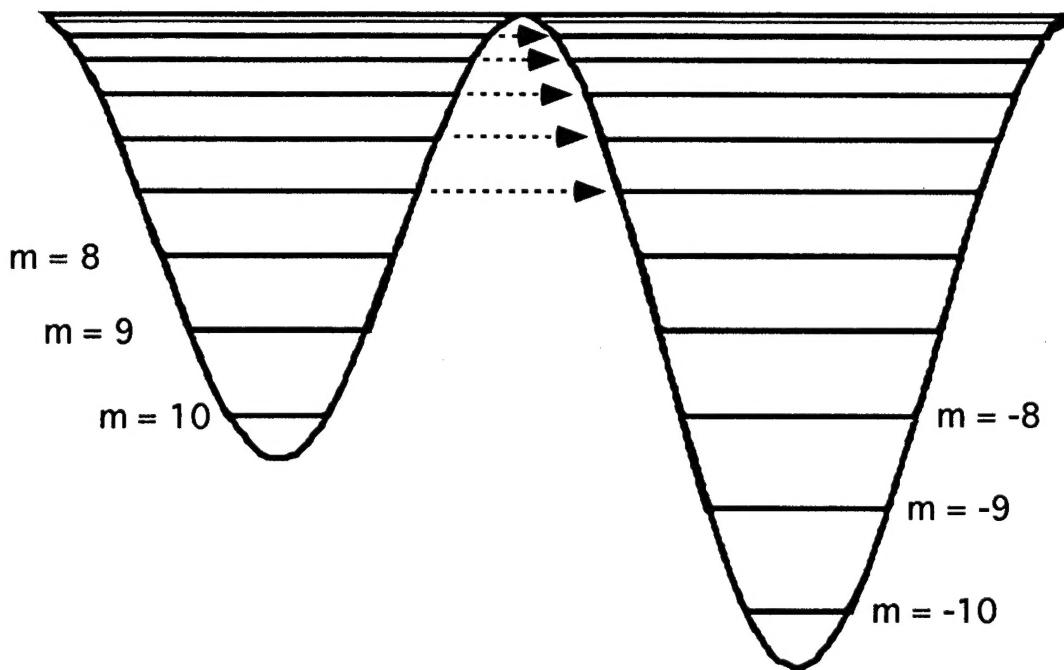


Figure 2

ground states separated by an anisotropy barrier, corresponding to spin parallel ($m = S$) or antiparallel ($m = -S$) to the c axis; a magnetic field breaks the symmetry making one state a true ground state. In Fig. 2 the system is shown initially populated in the metastable $m = S$ ground state in the left-hand well. When an applied field makes this state resonant with an excited

level in the right-hand well, transitions across the barrier are induced, followed by rapid spontaneous decay from the excited state to the ground state. We propose that each step in the magnetization corresponds to such a resonance. We claim further that our observation of discrete behavior in a sample of macroscopic dimensions is the result of resonant tunneling in a large number of chemically and magnetically identical molecules.

Magnetic molecules of this type are of great interest from a fundamental point of view. They are also interesting from a practical standpoint for several reasons. They may prove useful as microscopic memory units in extremely small computers and, in particular, in the quantum computers that have received a great deal of recent theoretical attention. Moreover, the energy difference between adjacent energy levels near the bottom of the potential well (see Fig. 2) is on the order of Terahertz. These molecules may thus serve as a source of terahertz radiation, an important region of the electromagnetic spectrum where few convenient sources are available.

b) Studies of magnetic properties of horse-spleen ferritin: Bull. Am. Phys. Soc. March, 1996.

Horse-spleen ferritin is an iron-storage protein with an inorganic antiferromagnetic core of diameter \approx 80 Angstroms. Recent experimental studies (D.D. Awschalom, *et al.*, Science 258, 414-421 (1992); J. Tejada *et al.*, J. Phys.: Cond. Matt. 6 (1), 263-266 (1994)) have reported that ferritin exhibits macroscopic quantum-mechanical effects at low temperatures. We have studied the dependence on magnetic field of the superparamagnetic blocking temperature of natural horse-spleen ferritin. Unlike most superparamagnetic materials where the blocking temperature decreases with applied field, we find that it increases from approximately 11 K at 5 mT to about 14 K at 0.3 T. At fields higher than 0.3 T, the blocking temperature decreases rapidly as a function of field, as expected. We also find that the hysteresis loop of ferritin at 12K is "pinched" (almost closed) near zero field. These data are consistent with an effective energy barrier that is smaller at low values of magnetic field. On the other hand, measurements of magnetic viscosity as a function of magnetic field, taken at both 5 K and 12 K, show no anomaly near zero field. In light of the important findings regarding this material, our results bear further careful attention and investigation.

THEORY:

Professor Eugene Chudnovsky completed a number of theoretical projects. These include a study of tunneling in random magnets, the introduction of the concept of a "critical state", studies of antiferromagnetic grains, and the crossover from antiferromagnetic to ferromagnetic tunneling. He has been invited to give a number of invited talks which also resulted in published papers. This work is described in more detail below:

a) Tunneling in random magnets: Phys. Rev. B 47, 9102 (1993).

It has been demonstrated experimentally (by Tejada and coworkers, Jour. Appl. Phys. 73, 6709 (1995), Arnaudas et al. and others) that rare earth-based random magnets exhibit non-thermal magnetic relaxation at low temperatures. For example, the magnetic viscosity of Tb-Fe amorphous alloys is proportional to temperature above 6K and is constant below 6K down to the lowest measured temperature of 1.8K. This low-temperature relaxation has been attributed to quantum tunneling out of metastable spin configurations. At first sight, it may seem difficult to determine a single tunneling variable in random magnets and spin glasses, similar to the total moment in small magnetic grains or the coordinate of a domain wall in magnetic crystals. Chudnovsky demonstrated, however, that such a variable can be rigorously introduced, based on the isotropy of the random spin system. It is the vector field which carries

out a parametrization of the group of spin rotations. The tunneling rate, $\Gamma = A \exp(-B)$ was calculated, where

$$A \approx \gamma (K/\chi)^{1/2} B^{1/2}, \quad B \approx (K\chi)^{1/2} \delta/\mu_B$$

and $\delta = (A_{ex}/K)^{1/2}$, γ is the gyromagnetic ratio, χ is the susceptibility, K and A_{ex} are average local anisotropy and exchange constants, respectively. For typical values $K \approx 10^9$ erg/cm³, $\chi \approx 10^{-2}$, and $\delta \approx 10^{-7}$ cm, this yields $A \approx 10^{12}$ s⁻¹ and $B \approx 30$, a tunneling rate large enough to give a significant magnetic relaxation. As many as 1000 spins are involved in individual tunneling events. The crossover from thermal to quantum relaxation occurs at

$$T_c \approx (\mu_B/k_B) (K/\chi)^{1/2}$$

which is of the order of a few Kelvin, in agreement with experiment.

b) The critical state: J. Appl. Phys. 73, 6697 (1993).

The concept of a magnetic critical state was introduced by Chudnovsky to explain the $\log(t)$ magnetic relaxation in bulk materials. When the external magnetic field is suddenly changed, the magnetization quickly attains the

value determined by the hysteresis curve. At this value, the local internal magnetic field is such that local energy barriers just begin to develop. This state can be viewed as an analog of Bean's critical state in superconductors, with domain walls playing the role of flux lines. The magnetic force on domain walls in the critical state is balanced by the pinning force. Detailed analysis of this model shows two important things. First, the condition of small barriers needed for tunneling is automatically satisfied in the critical state, without the fine tuning of the magnetic field which is required for a small magnetic grain, for example. Second, the slow departure from the critical state occurs via $\log(t)$ magnetic relaxation. The magnetic viscosity is proportional to temperature in the thermal regime and independent of temperature in the quantum regime, in accordance with experimental observations.

c) Tunneling in antiferromagnets: J. of Magn. Magn. Mat. **140-144**, 1821 (1995).

Barbara and Chudnovsky (Phys. Lett. A **145**, 205 (1990) demonstrated that tunneling is much stronger in antiferromagnets than in ferromagnets. The Neel vector, however, does not couple to the magnetic field. In order to observe antiferromagnetic tunneling, a small net magnetic moment is needed. In antiferromagnetic grains this is provided by a non-compensation of the sublattices due to the asymmetry of the grain that is generally present. In bulk antiferromagnets, a small moment often arises from canting of the sublattices, referred to as Dzyaloshinsky weak ferromagnetism. The important question here is how large the moment can be before the antiferromagnetic tunneling crosses to a much weaker ferromagnetic tunneling. This has been studied in terms of interacting antiferromagnetic sublattices. For small grains the critical non-compensation per unit volume turns out to be (χK) , which is about 1% for typical values of the susceptibility, χ , and anisotropy, K . We demonstrated that quantum tunneling of domain walls in weak ferromagnets is governed by antiferromagnetic dynamics. The crossover from thermal to quantum depinning of domain walls occurs at $T_c \approx hv_0/\delta$, where v and δ are, respectively, the limiting velocity and the thickness of the domain wall. Typical numbers provide a crossover at a few degrees Kelvin.

Publication in Reviewed Journals

J. R. Friedman, M. P. Sarachik, J. Tejada, J. Maciejewski, and R. Ziolo, to appear in *Jour. Appl. Phys.* April, 1996.

J. R. Friedman, M. P. Sarachik, J. Tejada, and R. Ziolo, submitted to *Phys. Rev. Letters*.

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Eugene M. Chudnovsky, *J. Appl. Phys.* **73**, 6697 (1993).

Eugene M. Chudnovsky, *J. of Magn. Magn. Mat.* **140-144**, 1821 (1995)..

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Invited Talks Sponsored by this Grant

1. "Macroscopic Quantum Tunneling of the Magnetic Moment," *MMM-37 Conference*, Houston, Texas, 1-4 December 1992.
2. "Macroscopic Quantum Tunneling in Magnets," *LT-20 Conference*, Eugene, Oregon, 4-11 August 1993.
3. "Magnetic Tunneling," *ICM-94 Conference*, Warsaw, Poland, 22-26 August 1994
4. "Theory of MQT in Magnetic Particles," *Int. Symposium on Magnetism in Lower Dimensions*, Wak, Japan, October 7-8 1994.